Ultrasonic Determination of the Pressure Dependence of the Superconducting Energy Gap in Tin*

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The effect of hydrostatic pressures to 3.3 kbar on the superconducting energy gaps in Sn is determined by measuring the longitudinal ultrasonic attenuation for propagation along [110], [100], and [001] directions. The extreme weak-coupling-limit prediction of the BCS theory that the volume dependence of the energy gap at absolute zero is equal to the volume dependence of the transition temperature is experimentally verified for Sn.

INTRODUCTION

THE Bardeen-Cooper-Schrieffer[1] (BCS) microscopic theory for superconductivity has enjoyed immense success in accounting for the observable properties of superconductors, particularly for those metals where the electron–phonon coupling is weak. One of the predictions of the BCS theory is that the superconducting energy gap and the critical temperature are linearly related. It is well known that the application of hydrostatic pressure to a superconductor can produce a shift in the critical temperature. Thus a measurement of the superconducting energy gap as a function of pressure provides an experimental test of this prediction of the BCS theory. In this paper we present energy gap measurements for metallic "white" Sn, determined by means of ultrasonic attenuation, as a function of hydrostatic pressure to ~3.5 kbar. Our results[2] show that for longitudinal sound propagating along the [001], [110], and [100] crystal axes, the change in the energy gaps is linearly related to the change in the critical temperature and the BCS prediction thus holds in Sn.

BACKGROUND MATERIAL

For a superconductor in the extreme weak-coupling limit, $T_c/\theta_D \to 0$ (where T_c is the superconducting transition temperature and θ_D is the Debye temperature), the BCS theory predicts that the energy gap at absolute zero, Δ_0, will obey the relation

$$2\Delta_0/kT_c = 3.53, \tag{1}$$

where k is Boltzmann's constant. It then follows that the volume dependence of the gap will be given by

$$d(\ln\Delta_0)/d(\ln V) = d(\ln T_c)/d(\ln V). \tag{2}$$

The BCS theory also relates Δ_0 to the critical field at absolute zero, H_0, and the electronic specific-heat coefficient γ by the relation

$$\Delta_0 = kH_0(\pi/6\gamma)^{1/2}. \tag{3}$$

This leads to an expression for the volume dependence of Δ_0 in terms of quantities derivable from critical-field measurements under pressure given by

$$d(\ln\Delta_0)/d(\ln V) = d(\ln H_0)/d(\ln V) - \tfrac{1}{2}d(\ln\gamma)/d(\ln V). \tag{4}$$

An attempt by Schirber and Swenson[3] to use Eqs. (2) and (4) to check the BCS prediction for the volume dependence of Δ_0 for α- and β-Hg, Sn, and Ta indicated that the combined experiment uncertainties in the pressure derivatives of H_0, γ, and T_c were too large to draw quantitative conclusions from available data.

Recently, Franck and Keeler[4] have made direct measurements of the effect of pressure on Δ_0 in Pb by tunneling experiments on polycrystalline thin films. These investigators find that the gap in Pb decreases with pressure at a rate about *twice* that of T_c and tentatively attribute this lack of agreement with Eq. (2) to the strong-coupling character of Pb.

Superconducting energy gaps in single crystals can be obtained, within the framework of the BCS theory, from measurements of the attenuation of longitudinal ultrasound as a function of temperature. The attenuations in the superconducting and normal states (α_s and α_n, respectively) are related to the energy gap as a function of temperature for $T \leq T_c$ by

$$\alpha_s/\alpha_n = 2[\exp(\Delta(T)/kT)+1]^{-1}. \tag{5}$$

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† Consultant, Sandia Laboratory.
[1] J. Bardeen, L. N. Cooper, and J. R. Schreiffer, Phys. Rev. **108**, 1175 (1957).
[2] Preliminary results of this work were reported by A. G. Beattie, J. E. Schirber, and J. R. Neighbors, Bull. Am. Phys. Soc. **12**, 416 (1967).
[3] J. E. Schriber and C. A. Swenson, Phys. Rev. **123**, 1115 (1961).
[4] J. P. Franck and W. J. Keeler, Phys. Rev. Letters **20**, 379 (1968). *Note added in Proof:* Additional studies of tunneling under pressure in lead have been reported by A. A. Galkin and V. M. Svistunov, Phys. Status Solidi **26**, K55 (1968); and V. N. Zararitskii, E. S. Itskevich, and A. N. Voronovskii, Zh. Experim. i Teor. Fiz. Pisma v Redaksiyu **7**, 271 (1968) [English transl.: JETP Letters **7**, 711 (1968)].

Analysis of experimental data using Eq. (5) often gives results for $2\Delta_0/kT_c$ which differ from the value of 3.53 predicted in Eq. (1). In these cases, Eq. (1) is replaced by

$$2\Delta_0/kT_c=G, \tag{6}$$

where G is the experimentally determined value. Other investigators[5–8] have shown an anisotropy in G for Sn with values ranging from 3.15 for propagation along a [001] axis to 3.96 for propagation along a [110] axis.

Tunneling experiments by Zavaritskii[9] have indicated that instead of a single energy gap, as is assumed in Eq. (5), Sn may have as many as 4 gaps in some directions. A simple extension of Eq. (5) to several gaps, assuming no interaction between the bands giving rise to the various gaps, is to write

$$\alpha_s/\alpha_n=\sum_i A_i[\exp(\Delta_i/kT)+1]^{-1}, \tag{7}$$

where $\sum_i A_i=2$. Claiborne and Einspruch[7] have shown that attenuation curves in Sn can be fit with two gaps using Eq. (7). However, as they recognize, the presence of several energy gaps makes the use of Eq. (7) in data analysis somewhat dubious since neither the number of gaps nor the relative values of the A_i are known. Therefore, in the experiments reported here, Eq. (5) has been used in the data analysis. It is recognized that this experiment does not *directly* measure the energy gaps. The gap parameter G is assumed to be an average of the various gaps which differs for each direction of propagation. Thus a measure of the volume dependence of G is a measure of the volume dependence of an average of the gaps for the given propagation direction.

EXPERIMENTAL DETAILS

Three samples were cut by spark erosion from a tin single crystal grown in this laboratory from Cominco stock. During magneto-resistance experiments on samples cut from this crystal, it was determined that the residual resistivity ratios were well in excess of 10^4. The samples were right circular cylinders, 8 mm in diameter and 2–6 mm in length, cut with [100], [110], and [001] crystal axes within 1° of the cylinder axis. The end faces of the cylinders were finished by spark planing. These faces were aligned to within ½° of the desired crystal planes as shown by back-reflection Laue pictures of the finished faces.

The ultrasonic attenuation was measured with longitudinal waves at 90 MHz using standard pulse-echo techniques. A boxcar integrator allowed the continuous recording of a particular echo amplitude as a function of temperature. An external rf pulse was passed through a calibrated attenuator into the receiver and the system was calibrated in this manner on every experimental run. Data for propagation along the [001] and [110] axes were taken with samples about 6 mm long, which was long enough to separate the echoes in time. The change in the attenuation in these samples was about 30 dB per cm. To increase the receiver sensitivity, synchronous detection was used. The attenuation for propagation down a [100] axis was too large to allow a sample of sufficient length to separate the echoes. Therefore an X-cut quartz delay rod was used with this sample and the synchronous detection omitted. The transducers were X-cut quartz with a 10 MHz fundamental frequency. All acoustic bonds were made with Dow Corning 200 fluid of 200 000 centistoke viscosity.

Hydrostatic pressure up to about 3.5 kbar was applied to the sample using the solid-helium technique.[10] A diagram of the pressure bomb is shown in Fig. 1. This bomb had an o.d. of 2.54 cm and an i.d. of slightly over

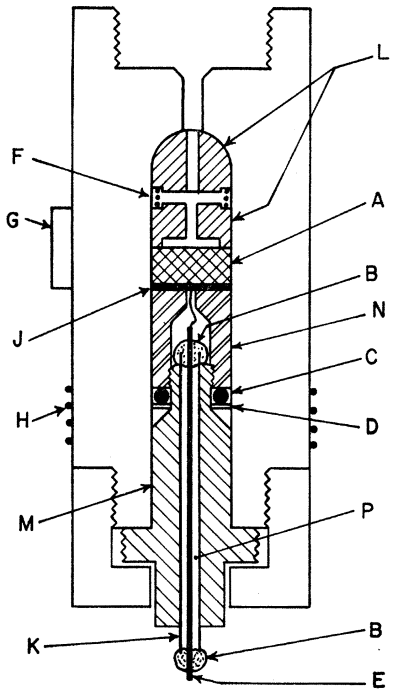

FIG. 1. Schematic view of hardened Be–Cu pressure bomb. A, sample; B, epoxy seal; C, O-ring; D, deformable Be-Cu washer; E, copper wire; F, spring; G, Ge resistance thermometer; H, heater; J, transducer; K, stainless-steel tube; L, brass void fillers; M, stainless-steel plug; N, phenolic void filler and seal puller; P, MgO insulation.

[5] R. W. Morse, T. Olsen, and J. D. Gavenda, Phys. Rev. Letters **3**, 15 (1959); R. W. Morse, T. Olsen, and J. D. Gavenda, Phys. Rev. Letters **3**, 193 (1959).

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[7] L. T. Claiborne and N. G. Einspruch, Phys. Rev. **151**, 229 (1966).

[8] J. M. Perz and E. R. Dobbs, Proc. Roy. Soc. (London) **A297**, 408 (1967).

[9] N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **48**, 837 (1965) [English transl.: Soviet Phys.—JETP **21**, 557 (1965)].

[10] J. E. Schirber, in *Proceedings of the First International Conference on the Physics of Solids, Arizona, 1965*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York. 1966).

8 mm. It was constructed of hardened beryllium copper and used an unsupported area seal for the closure at the bottom. Details of the closure and the epoxy-sealed rf lead-in are published elsewhere.[11] The sample was used as the ground potential electrode for the transducer, and good electrical contact between the sample and the bomb was provided by the spring-loaded brass plugs. As is shown in Fig. 1, the acoustic wave was reflected either from a tin-helium or from a quartz-helium interface to provide a large echo amplitude.

Temperatures were measured with a germanium resistance thermometer placed in thermal contact with the bomb. The voltage across this thermometer could either be read with a potentiometer or applied to one axis of an X-Y recorder. A simple field effect transistor circuit[12] was used to maintain a constant current through the thermometer as the temperature changed. The thermometer was calibrated with respect to the vapor pressure of helium using the T_{58} temperature scale.[13] A series of calibration points was fit to an empirical formula and a complete calibration curve then calculated. It is estimated that the calibration was accurate to better than 5 mdeg between 1.1 and 2.2°K. All data were taken as the temperature was decreased. The minimum temperature that could be reached in the cryostat was 1.12°K.

In making an experimental run, the bomb was first loaded with the sample and then flushed with helium gas several times. The bomb was then pumped up to about 4 kbar to deform the softened Be-Cu washer of the seal. After testing for leaks, the pressure was maintained at the desired value and the bomb slowly lowered in a cryostat containing liquid helium. The very gradual lowering ensured that isobaric freezing of the fluid helium occurred from the bottom up. Further cooling of the bomb was by controlled pumping on the helium in the cryostat. The average time taken to make an experimental run, i.e., cool down from 4.0 to 1.12°K, was about 2h. The normal experimental sequence was "zero pressure," then pressure runs with an occasional "zero pressure"-pressure-"zero pressure" sequence to check possible pressure damage to the sample. No evidence of damage was seen. A minimum of two identical runs were taken at each pressure to check experimental reproducibility. Experimental runs that have been designated "zero pressure" were actually taken at a pressure of about 0.30 kbar. This was to ensure that all data were taken with the helium frozen so that the sample and transducers always experienced a similar environment.

Isobaric measurements as a function of temperature of relative echo heights (and therefore attenuation) were taken for the three directions of propagation. For the [110] and [001] directions, the outputs of the boxcar integrator and the thermometer were connected to an X-Y recorder and tabular data were read from the resulting graphs. For the [100] high-attenuation sample, the data were taken point by point. Since beryllium copper is a poor thermal conductor and the thermometer was on the exterior of the bomb, the pumped bath temperature had to be changed slowly in order to ensure thermal equilibrium between the thermometer and the sample. To avoid the possibility of temperature gradients along the bomb, only data below the λ point of helium were used in computing the energy gaps. The necessity of slowly varying the temperature imposes stringent stability requirements upon the electronics. Lack of stability, apparent as small long-term drifts in the electronic gain, and not the accuracy with which the attenuation could be calibrated and measured (better than ± 0.01 dB), limited the reproducibility of the experimentally determined value of G. The thermometer was not placed inside the bomb since this procedure would require four additional leads and the effect of pressure on the resistance thermometer calibration would need to have been determined.

DATA ANALYSIS AND RESULTS

Equation (5) gives a relation between the temperature-dependent energy gap $\Delta(T)$ and the electronic components of the ultrasonic attenuation in the superconducting and normal states. Experimentally, the quantity measured is the sum of the electronic and lattice contributions to the attenuation. Since the electronic component of the attenuation essentially vanishes for values of $T/T_c \leq 0.2$, a measurement of the attenuation in this range would constitute a measurement of the lattice attenuation α_0. However, for Sn, this requires temperatures ($T \sim 0.7$°K) not attainable in a ^{4}He cryostat. Therefore, as in most previous attenuation measurements of a gap, it was necessary to estimate α_0. To do this, it was assumed that Eq. (5) gave a good approximation to the experimental curve and a computer was programmed to search through a range of α_0 until a value was found which gave a best fit of the data to the theoretical curve.

To analyze the data using Eq. (5), $\Delta(T)$ can be expressed as

$$2\Delta(T)/kT_c = GM(T), \tag{8}$$

where $M(T)$ is the temperature dependence of the gap. Muhlschlegel[14] has calculated $M(T)$ from the BCS theory and presented the results in tabular form. This table was used in a preliminary treatment of the data but, in a computer analysis, it is desirable to use analytic functions if possible. Sheahen[15] has shown that a good approximation to the BCS temperature dependence is $M(T) = \{\cos[\frac{1}{2}\pi(T/T_c)^2]\}^{1/2}$. When data were ana-

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[15] T. P. Sheahan, Phys. Rev. **149**, 368 (1966).

TABLE I. Experimental values of the energy gap parameter G and the percentage changes with pressure of Δ_0 and T_c.

Investigation	Pressure (bar)	Direction of acoustic propagation [001]	[110]	[100]
Claiborne and Einspruch[a]	~1	3.26±0.02	3.94±0.04	3.62±0.04
Perz and Dobbs[b]	~1	3.15±0.04	3.84±0.07	3.55±0.07
This work	300	3.19±0.05	3.86±0.04	3.48±0.04
This work	3300	3.17±0.02	3.89±0.05	3.50±0.04
		% change with 3.3 kbar		
Δ_0		4.6±1.6%	3.3±1.8%	3.5±1.4%
T_c		4.3±0.2%[c]	4.3±0.2%[c]	4.3±0.2%[c]

[a] See Ref. 7.
[b] See Ref. 8.
[c] See Ref. 16.

lyzed with this function in place of the Muhlschlegel values, the value of G found from the best fit of the data to Eq. (5) decreased by about 0.1%. This decrease is not significant when compared to the experimental error, so the Sheahen approximation was used in all data analysis.

Equations (5) and (8) were combined, using the Sheahen approximation to obtain

$$G=\frac{2T}{T_c\{\cos[\frac{1}{2}\pi(T/T_c)^2]\}^{1/2}}\ln\left[\frac{2\alpha_N(T_c)-2\alpha_0}{\alpha_S(T)-\alpha_0}-1\right], \quad (9)$$

where $\alpha_N(T_c)=\alpha_n(T_c)+\alpha_0$ and $\alpha_S(T)=\alpha_s(T)+\alpha_0$ are the experimentally determined values of the attenuation. A value for T_c of 3.722°K was used at atmospheric pressure. While T_c was determined at each pressure, the accuracy of the measurements was not as great as that of Jennings and Swenson[16] so their value of dT_c/dP was used to compute T_c at the pressures used. With input data of T_c, $\alpha_N(T_c)$, and $\alpha_S(T)$, the computer searched through a range of α_0 until it found the value which gave the best fit to Eq. (9). This determined the value G for that particular run. In Fig. 2, a fit of the data points to Eq. (5) is shown using the computer-determined value of α_0. The final results are averages of the G values for many runs and are given in Table I. Also included in Table I are G values for Sn determined by Claiborne and Einspruch[7] and by Perz and Dobbs.[8] The three sets of G values are in fair agreement. The percentage changes with pressure in the average of the energy gaps $\bar{\Delta}_0$ seen in each propagation direction were calculated using Eq. (6) and are compared in Table I with the percentage change with pressure of T_c. As can be seen, the change in each $\bar{\Delta}_0$ is the same as the change in T_c to within experimental error.

The major source of error in this experiment stems from the compromise required between the necessity of cooling slowly enough to maintain thermal equilibrium between the sample and the thermometer and the occurrence of long-term drifts in the electronic gain. The resulting errors in the temperature and the attenuation led to erroneous values of G when the curves were analyzed, even though the data appeared to be quite good. It is estimated that most of the errors quoted in Table I arose from this source. The few obviously wrong values of G were thrown out with all others being included in the averages.

Another source of error in analysis is that, since Sn is a multigap superconductor, the experimental curve has a systematically different shape from that predicted by Eq. (5). This difference can be most readily seen for the large values of T/T_c in Fig. 2. The result of this deviation is that the value of G obtained from Eq. (9) is affected by the range in T/T_c over which the data are analyzed. To ensure uniformity in analysis, only data over the range $0.32\leq T/T_c\leq 0.58$ were used. This dependence upon the range of data used probably

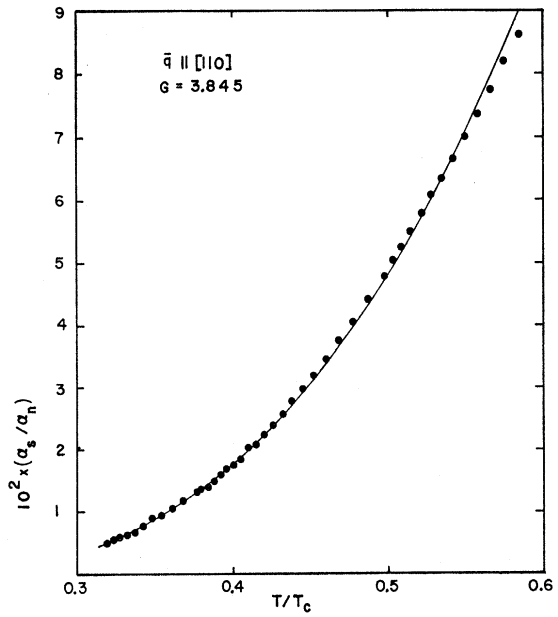

FIG. 2. Plot of the best-fit BCS curve and data for a "zero pressure" run with the direction of propagation along a [110] axis. The computer-determined value of α_0 has been subtracted from the experimental values α_N and α_S.

[16] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).

accounts for the small differences in the values of G reported by Claiborne and Einspruch,[7] by Perz and Dobbs,[8] and in this experiment.

In Eq. (9), $\alpha_N(T_c)$ has been used instead of the correct quantity $\alpha_N(T)$. If the temperature is well into the region where the sample shows impurity-limited conductivity, this procedure is valid. Otherwise, it can lead to small errors. A measurement of this temperature dependence for our samples was made in a 400-G field and showed a maximum change between 3.72 and 2.0°K of 0.3 dB/cm, with no change below 2.0°K. This change will produce an error in the value of G obtained from our analysis of less than 0.2%, which is considerably less than the experimental reproducibility in the values of G.

CONCLUSIONS

Ultrasonic attenuation measurements of the superconducting energy gaps in Sn have been made as a function of hydrostatic pressure. The "zero pressure" measurements of the gap parameter G for propagation down to [100], [110], and [001] crystal axes are in fair agreement with previous measurements. While the multigap character of Sn prevents the direct measurement of a single energy gap, three separate averages over the energy gaps could be measured. The pressure dependence of each of these averages was the same, within experimental error, as the pressure dependence of T_c. Thus we conclude that the linear relation between the energy gap and the critical temperature predicted by the BCS theory holds for the weak-coupled superconductor Sn.

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Observation of Pair Interaction between Ortho Molecules in Solid H_2†

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A study of the electric quadrupole-quadrupole (EQQ) interaction between ortho-H_2 molecules in solid H_2 is presented. This work consists in recording and interpreting the pair spectrum of proton nuclear magnetic resonance for low ortho-H_2 concentrations. In the theoretical part of this paper, a calculation of the absorption spectrum for an isolated pair of ortho molecules is presented, and the temperature dependence of this spectrum is derived as a function of the rotational states of the isolated ortho pair. Furthermore, the results of similar calculations on the absorption spectrum of isolated triangles of ortho-H_2 molecules in solid H_2 are briefly discussed. This spectrum is expected to be less pronounced than the pair spectrum and to be mostly responsible for a broad absorption background. The experimental work, carried out at temperatures between 0.45 and 14°K on several low ortho-H_2 concentrations shows the maxima expected from theory. From the analysis of the results, and assuming the interactions between molecules to be purely EQQ, the coupling constant $\Gamma/k_B=6e^2Q^2/25R^5k_B$ is found to be 0.82°K. This value is smaller than that expected for the solid rigid lattice, where $\Gamma/k_B=1.00$°K. One also obtains from the analysis a dipolar coupling constant $d=54.5$ kHz which is smaller than that measured for the free H_2 molecule, where $d=57.7$ kHz. It is suggested that the departures both in Γ and in d from expectations are caused by the interactions between lattice vibrations and rotations, since solid H_2 will behave more like a quantum crystal with large zero-point motion than like a classical rigid crystal.

I. INTRODUCTION

THE orientational state of solid alloys of ortho-para hydrogen has been studied by many authors. For most applications one assumes that J is a good quantum number: $J=0$ for para molecules and $J=1$ for ortho molecules. Accordingly, to describe the orientational state of ortho-para alloys one need consider only the removal of degeneracy of the ortho molecules. In this connection, Nakamura[1] was the first to show that the electric quadrupole-quadrupole (EQQ) interaction is the most important orientationally dependent term in the intermolecular potential. This interaction is

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